

Strontium Isotopic Identification of Water-Rock Interaction and Ground Water Mixing

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Abstract

⁸⁷Sr/⁸⁶Sr ratios of ground waters in the Bighorn and Laramie basins' carbonate and carbonate-cemented aquifer systems, Wyoming, United States, reflect the distinctive strontium isotope signatures of the minerals in their respective aquifers. Well water samples from the Madison Aquifer (Bighorn Basin) have strontium isotopic ratios that match their carbonate host rocks. Casper Aquifer ground waters (Laramie Basin) have strontium isotopic ratios that differ from the bulk host rock; however, stepwise leaching of Casper Sandstone indicates that most of the strontium in Casper Aquifer ground waters is acquired from preferential dissolution of carbonate cement. Strontium isotope data from both Bighorn and Laramie basins, along with dye tracing experiments in the Bighorn Basin and tritium data from the Laramie Basin, suggest that waters in carbonate or carbonate-cemented aquifers acquire their strontium isotope composition very quickly—on the order of decades.

Strontium isotopes were also used successfully to verify previously identified mixed Redbeds-Casper ground waters in the Laramie Basin. The strontium isotopic compositions of ground waters near Precambrian outcrops also suggest previously unrecognized mixing between Casper and Precambrian aquifers. These results demonstrate the utility of strontium isotopic ratio data in identifying ground water sources and aquifer interactions.

Introduction

Many hydrogeologic processes involve mixing of waters of different chemical and/or isotopic compositions. If unrecognized, mixing of waters from different aquifers results in inaccurate determination of water ages, flow directions, and aquifer yields, among other parameters (Mazor et al. 1993). Strontium isotopes are useful fingerprints of ground water and tracers of ground water mixing; they have been used to characterize brines and formation waters associated with oilfield reservoirs (Chauduri et al. 1987; McNutt et al. 1990; Smalley et al. 1992; Lyons et al. 1995) and fresh water hydrologic systems (Collerson et al. 1988; Banner et al. 1994; Armstrong et al. 1998; Gosselin

et al. 2001; Frost et al. 2002). The precision of the strontium isotopic tracer allows for detection of small variations in ground water strontium isotope composition. Moreover, the isotope ratio is not affected by fractionation or by mineral precipitation. The strontium isotopic composition of water is dependent only upon dissolution of minerals and ion exchange reactions; as water flows through an aquifer, it progressively acquires an ⁸⁷Sr/⁸⁶Sr ratio from the rocks with which it interacts.

This study uses strontium isotopic data to characterize ground waters present in the Laramie and Bighorn basins, where aquifers are chemically and hydrologically well characterized (Lundy 1978; Huntoon and Lundy 1979; Huntoon 1985; Younus 1992; Mazor et al. 1993). This study addresses three questions regarding the applicability of strontium isotope ratio identification of ground water-rock interaction and ground water mixing. (1) Do different aquifers impart distinctive strontium isotopic ratios to their ground waters, and which components of aquifer rocks contribute to the ⁸⁷Sr/⁸⁶Sr ratio of ground water? (2) What is the timescale by which strontium is imparted from carbonate or carbonate-cemented rocks to waters? (3) Can

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ground water mixing be identified using strontium isotopic data?

Geologic Setting

The Bighorn Basin of north-central Wyoming is a large intermontane basin that is bounded on the west by the Absaroka Mountains, on the south by the Owl Creek Mountains, and on the east by the Bighorn Mountains. The study area encompasses ~500 km² in the Bighorn Basin near the town of Hyattville (Figure 1). The basin within this region consists of more than 850 m of Cambrian to Pennsylvanian age shales, sandstones, limestones, and dolomites. The two primary aquifers in the study area are the Madison Aquifer and the Tensleep Aquifer. Both aquifers are exposed along the western edge of the Bighorn Mountains and dip westward into the basin. The Pennsylvanian Tensleep Sandstone is a massive, fine-grained, cross-bedded eolian sandstone that in places has been reworked by shallow seas (Darton 1906; Boyd 1993). The framework grains are dominated by quartz (82% to 93%) with lesser alkali feldspar; they are cemented with silica, anhydrite, and calcite (Mankiewicz and Steidtmann 1979). It is highly permeable, contributing to its viability as a regional aquifer (Vietti 1977). The Madison Aquifer is

comprised of the Ordovician Bighorn Dolomite, the Devonian Jefferson Limestone, and the Mississippian Madison Limestone, all of which are marine carbonates hydraulically connected by joints and fractures (Huntoon 1985). In addition, a karst cave system in the limestone and dolomite first developed during Mississippian regression increases permeabilities throughout the Madison Aquifer (Huntoon 1985). The Madison and Tensleep aquifers are separated by the Amsden Formation, which is a sequence of gray, cross-bedded sandstones, red shales, and cherty limestones (Darton 1906). Differences in wellheads and major ion chemistry between the two aquifers suggest that the Amsden Formation is an effective confining unit (Huntoon 1985).

The second study area includes a 550 km² portion of the Laramie Basin along the western flank of the Laramie Mountains, Wyoming. There are three aquifers in the area: the Redbeds Group, the Casper Formation, and the Precambrian basement. The Casper Formation and the Redbeds strike north-south and dip 2° to 8° westward into the basin (Lundy 1978). Based on decreases in wellheads from east to west, ground water flow is generally westward (Mazor et al. 1993), except where fault planes intercept and divert flow (Figure 2) (Lundy 1978).

Precambrian igneous and metamorphic rocks core the south-central Laramie Mountains. Two Proterozoic units are exposed in this study area and define the eastern limit of the recharge area to the Laramie Basin aquifer system. The 1.76 Ga Horse Creek Anorthosite Complex (HCAC) is a small, ~100 km² series of anorthosite, monzonite, and granite intrusions that crop out in the extreme northeastern corner of the study area (Figure 2) (Frost et al. 2000). The 1.43 Ga Sherman Batholith is the second and dominant Precambrian unit in the study area. The batholith is dominated by the medium- to coarse-grained Sherman Granite (Frost et al. 1999). Because wells completed within the Precambrian are generally not very productive, previous authors have interpreted the Precambrian rocks as basal confining units for the overlying Casper Formation (Lundy 1978; Younus 1992; Mazor et al. 1993).

The Pennsylvanian-Permian Casper Formation is a series of interlayered sandstones and limestones that are time-correlative to the Tensleep Sandstone in central Wyoming. The fine-grained sandstones in the Laramie Basin are composed mainly of detrital quartz grains, with lesser amounts of feldspar (< 6%, 95% of which is potassium feldspar), and accessory minerals (Kirn 1972). They vary in color from light-brown to red and are cemented predominantly with calcite and dolomite, although micrite, silica, and hematite cements are present (Kirn 1972). Based on well water level data, Lundy (1978) considered five intervening limestones to be continuous, impermeable, confining layers for the sandstone reservoirs between them.

The overlying Redbeds Group ranges in age from Permian to Jurassic and includes five formations (Mazor et al. 1993). Shales and mudstones containing thin layers of sandstone, limestone, and gypsum dominate the Satanka and Chugwater formations (Chen and Boyd 1997). The Forelle Formation is a thin limestone unit separating the Satanka and Chugwater formations. Farther west, along the Laramie River, sandstones and shales of the Jurassic Sundance and

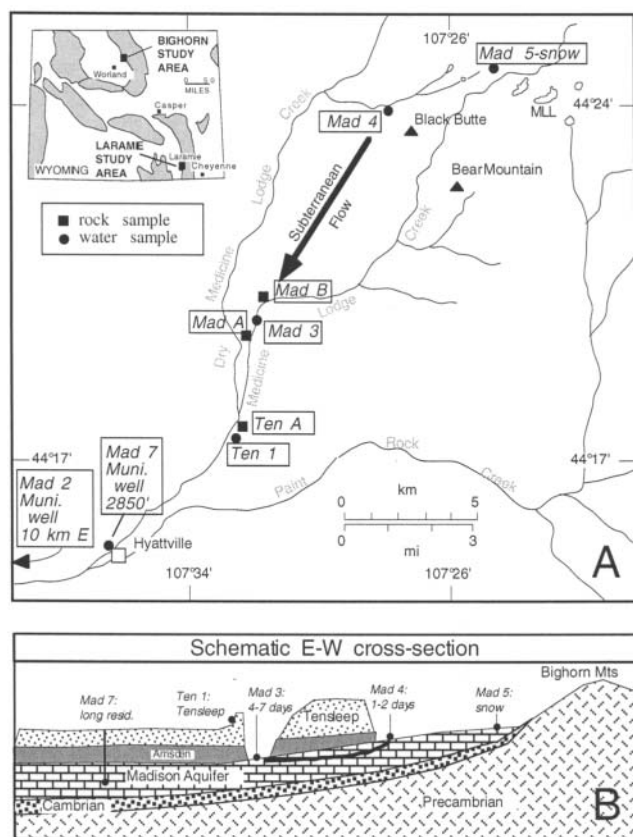


Figure 1. West flank of Bighorn Mountains, Wyoming. (a) Strontium isotope sample localities. Two additional samples were collected outside the map area, including Mad1 from a flowing spring discharging along the east side of the Bighorn River at Sheep Anticline north of Greybull 50 km northwest of the study area, and Mad2 from the Worland municipal wells located 10 km west of Hyattville, Wyoming. (b) Schematic cross section of flowpaths and approximate residence times of ground water samples.

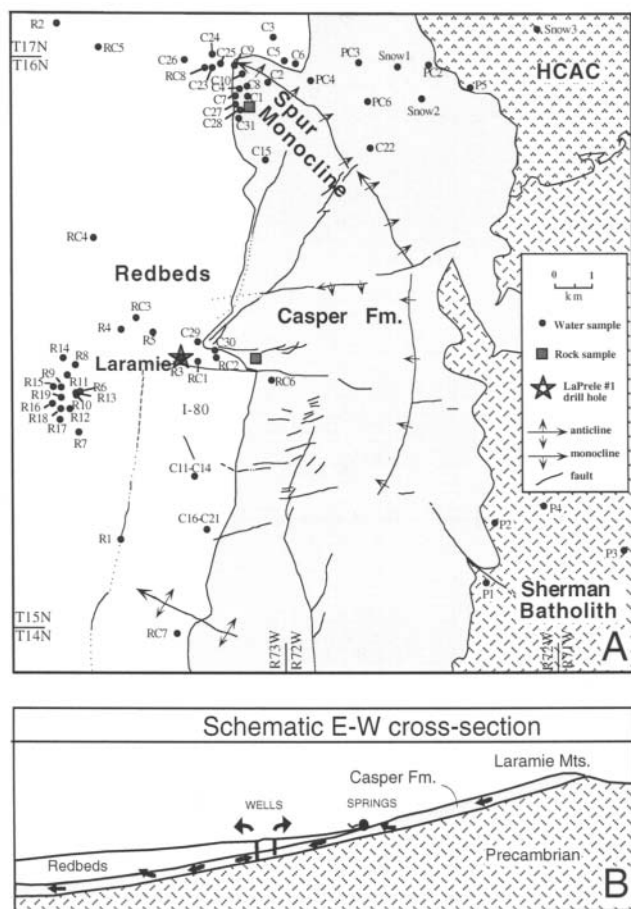


Figure 2. (a) Laramie Basin study area showing sample locations and regional geology (Lundy 1978). (b) Schematic cross section of Laramie Basin showing ground water flow direction and location of springs along Casper/Redbeds contacts.

Morrison formations are present. Because some wells completed in the Casper Formation are artesian, the Redbeds have been interpreted to be a confining layer for the Casper Formation aquifer system (Lundy 1978; Younus 1992; Mazor et al. 1993).

The Laramie Basin has undergone substantial structural activity, as evidenced by the numerous faults and folds in the region (Figure 2). Laramide reverse faults core many of the more prominent topographic features in the area, such as the Spur Monocline (Lundy 1978; Huntoon and Lundy 1979). Younger normal faults that truncate and offset the reverse faults are also present in the study area (Lundy 1978). Increased permeabilities and transmissivities of the aquifer rocks within the fracture zones focus and divert the otherwise westward flow of ground water along the variable trends of these faults (Lundy 1978; Huntoon and Lundy 1979). The faults also provide vertical hydraulic connections between distinct aquifers (Lundy 1978; Huntoon and Lundy 1979).

Sample Collection and Analytical Procedures

Water Samples

Wells and springs in the Bighorn and Laramie basins were sampled based upon their geographic locations and the aquifers from which they derive ground water. Waters

representative of the Madison Aquifer were sampled from wells and springs in the Bighorn Basin. In addition, snow and surface water samples were collected to characterize recharge; sample locations parallel a surface and subterranean flowpath in order to identify ground water evolution trends along this path (Figure 1). In addition, a sample from the overlying Tensleep Aquifer was collected to determine if waters from the two aquifers have distinct strontium isotope ratios.

In the Laramie Basin, sampled wells include those completed within Precambrian rocks (sample numbers prefixed with a "P"), the Casper Formation (sample numbers prefixed with a "C"), and Redbeds formations (sample numbers prefixed with an "R"). Wells which, based on completion records or proximity to faults or other structural features, probably yield mixed Precambrian-Casper waters were sampled and are identified with the prefix "PC." Likewise, wells identified by Lundy (1978) and Mazor et al. (1993) as producing mixed Casper-Redbeds water were also sampled, and given the prefix "RC" (Figure 2).

Eighty-four water samples were collected from municipal, domestic, and livestock wells throughout the Laramie and Bighorn basins. ~1 L of water was collected from each domestic and livestock well after it was flushed for ~20 minutes; no evacuation of casing was necessary prior to collecting water samples from continually pumped municipal wells. In the Laramie Basin, three water samples from local springs were also collected, along with one rain and three snow samples. One snow sample, one stream sample, and three spring waters were acquired from the Bighorn Basin. To minimize contamination, snow samples were collected 0.3 m below the snow surface directly into Teflon® containers and melted in the Class 100 clean room at the University of Wyoming. All samples were filtered through 0.45 µm filters and stored in acid-washed Nalgene® or Teflon bottles.

Acidified and untreated 60 mL aliquots were used for major cation and anion analysis, respectively. Major ions were analyzed by atomic absorption, ion chromatography, inductively coupled plasma-mass spectrometry, and acid-base titration procedures. Errors associated with major ion measurements typically range between ± 3% to 5% of the measured values, although alkalinity errors may be as low as ± 1% to 2%. Two 1 mL aliquots were also taken from each sample. One of these was spiked with an ^{84}Sr -enriched solution in order to determine the strontium concentration by isotopic dilution. The unspiked aliquot was used to determine the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Aliquots were evaporated, redissolved in 3.5M HNO_3 , and passed through Teflon columns filled with Eichrom Sr*Spec™ resin. Samples were analyzed for strontium isotopic composition on a VG Sector thermal ionization mass spectrometer at the University of Wyoming. The internal precision of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measurements is ± 0.00001. Thirty-five analyses of NBS987 strontium standard measured on the University of Wyoming's VG Sector thermal ionization mass spectrometer during the study gave an average value of $^{87}\text{Sr}/^{86}\text{Sr} = 0.71024 \pm 0.00004$ (2 standard deviations). All analyses were normalized to an $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.1194. Analytical blanks were 0.2 ng or lower, negligible compared to sample sizes of 0.1 to 1.0 µg strontium.

Tritium analyses were obtained on seven ground water samples collected in October 1996 from seven wells completed in the Casper Formation of the Laramie Basin. Analyses were performed at the University of Miami by proportional counting of H₂ gas derived from the water sample. The counters were operated in anticoincidence mode with a surrounding cosmic-ray detector system. Errors on the measurements are $< \pm 0.5$ TU.

Rock Samples

Rock samples from the Madison, Tensleep, Redbeds Group, Casper Formation, and Precambrian aquifers were analyzed for their strontium compositions. Redbeds and Casper Formation aquifer rocks were obtained from well cutting samples from LaPrele1 cores (Figure 2); other samples were collected from outcrops (Figures 1 and 2). Two dissolution procedures were used: bulk dissolution and stepwise leaching. For the bulk dissolutions, rock samples were powdered and ~0.1 g dissolved. A ⁸⁴Sr-enriched spike was added to an aliquot of the sample for strontium concentration measurements by isotopic dilution. The remaining unspiked portion was used for ⁸⁷Sr/⁸⁶Sr ratio analysis. Strontium was isolated using standard cation exchange chromatography. Strontium isotopic compositions were determined by thermal ionization mass spectrometry using the methods as for water samples. Strontium data for Laramie Basin Precambrian rocks were obtained from Frost et al. (1999) and Frost et al. (2000).

In order to determine which components of the rocks contribute strontium to ground water, a step-dissolution procedure was performed on outcrop samples of Casper Formation sandstone using a method adapted from Tessier et al. (1979). The coarsely crushed sandstone was first rinsed and tumbled in deionized water. A solution was then added to 100 g of the crushed sandstone and the resulting slurry was agitated for one hour. The mixture was centrifuged and the leach was drawn off by pipette. After being rinsed with deionized water three times and dried in an oven, 0.5 to 1.0 g of the sandstone was set aside for scanning electron microscope (SEM) analysis. The process was then repeated using the remaining sandstone and different reagents. 1M MgCl₂, 1M NaOAc, 0.1M HCl, and HF/concentrated HNO₃ solutions were used to extract exchangeable ions, carbonates, sulfides and carbonates, and silicates, respectively.

The leached fractions collected from each step were analyzed for their strontium concentrations and ⁸⁷Sr/⁸⁶Sr ratios using the cation chromatography and mass spectrometry methods described for water samples. Samples of rock residue collected after each step were imaged on the University of Wyoming's JEOL scanning electron microscope.

Results

Geochemical Character of Ground Waters

Major ion analyses of Bighorn Basin ground waters indicate that both Madison and Tensleep aquifer waters are calcium-bicarbonate type (Table 1). Tensleep waters collected from farther within the basin exhibit calcium-sulfate compositions (Jarvis 1986), suggesting that Tensleep water compositions are variable.

Laramie Basin ground water samples collected from the Casper Formation are calcium-bicarbonate to calcium-magnesium-bicarbonate type (Table 2). Ca-HCO₃ waters are derived from wells located within the exposed recharge area of the Casper Formation, whereas Ca-Mg-HCO₃ waters are from wells drilled through both the Redbeds and the Casper Formation (Lundy 1978). Modest variations in potassium (0.58 to 2.87 mg/L), sodium (1.49 to 5.08 mg/L), and chlorine (1.34 to 7.86 mg/L) concentrations in Casper ground water samples were interpreted by Mazar et al. (1993) as evidence that recharge to the aquifer occurs in isolated flow systems and that ground water moves through the aquifer in distinct zones, such as the subaquifers of the Casper Formation.

Ground waters from the Redbeds Aquifer exhibit strong calcium-magnesium-sulfate signatures (Table 2). The high magnesium, chlorine, calcium, and SO₄ concentrations of the Redbeds waters distinguish them from both Casper Formation and Precambrian ground waters (Figures 3). However, like the Casper Formation waters, Redbeds waters exhibit a range of sodium and potassium concentrations. These diverse values can again be attributed to different recharge systems and ground water storage within discrete zones of the Redbeds Aquifer system (Mazar et al. 1993).

Precambrian ground waters have calcium-bicarbonate compositions. They are distinguishable from Casper and Redbeds waters by their low magnesium concentrations

Table 1
Chemical Analyses of Eastern Bighorn Basin Ground Waters and Precipitation

Sample	Description	Well Depth (m)	Static Water Level (m)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Si (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	Alkalinity (meq/L)
Mad1	Spring, Sheep Anticline	1295	60	51.2	22.6	4.34	1.44	8.98	2.83	43.2	3.88
Mad2	Worland city well			39.2	22.0	2.57	1.20	5.51	0.75	13.01	3.73
Mad3	Spring			21.2	9.38	1.90	0.61	4.32	0.38	3.38	1.89
Mad4	Stream			8.28	3.00	1.92	0.53	4.19	0.39	2.85	0.778
Mad5	Snow	891	65	0.47	0.13	1.55	0.95	0.05	1.60	0.31	0.043
Mad7	Hyattville city well			52.5	24.1	4.32	1.89	4.51	1.45	54.9	3.91
Ten1	Spring			55.9	20.3	2.74	2.02	8.35	0.72	11.2	4.59

Well depth and static water level information from the Wyoming State Engineer, www.sco.state.wy.us

Table 2
Chemical Analyses of Laramie Basin Ground Waters and Precipitation

Sample	Location (Sec-Tw-Ra)	Date Collected	Well Depth (m)	Static Water Level (m)	Temper- ature	pH	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Si (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	Alk. (meq/L)	TDI (meq/L)
Redbeds Aquifer samples															
R1	NWN3 28-15-73	7/10/96	103	10	10.5	7.13	556.00	89.20	21.90	2.12	9.34	22.6	1497.00	3.57	71.98
R2	NWSE 29-17-73	5/19/98	51	12	9.8	6.86	220.11	103.52	51.61	3.64	7.72	30.50	868.77	2.21	51.13
R3	SENE 3-15-73	9/25/95	271	15	NA	NA	230.85	56.65	4.32	1.31	6.01	10.78	437.93	0.00	37.26
R4	NWSE 33-16-73	7/3/96	111	flowing	NA	7.25	153.00	65.20	12.6	1.86	8.47	4.27	476.00	3.12	27.16
R5	NESW 34-16-73	7/5/96	18	no data	14.7	6.87	267.00	63.90	14.3	1.92	8.45	18.9	666.00	3.35	37.75
Mixed Redbeds and Casper aquifers samples															
RC1	SENW 2-15-73	8/4/95	111	6	NA	NA	38.12	24.63	2.24	1.36	4.68	1.23	6.40	3.22	7.67
RC2	NWNE 2-15-73	9/9/95	170	12	NA	NA	47.16	22.62	1.40	0.70	4.45	2.04	6.59	3.48	8.22
RC3	SWNE 33-16-73	7/16/96	270	flowing	13.0	7.87	30.90	21.30	6.78	3.33	4.46	4.09	19.10	3.44	7.86
RC4a	NWSW 21-16-73	7/10/96	394	flowing	11.3	8.05	28.20	21.20	4.81	1.07	2.90	2.53	24.80	2.75	6.90
RC4b	NWSW 21-16-73	10/11/96	394	flowing	11.0	7.84	25.60	19.80	4.76	1.05	3.75	2.35	24.80	2.68	6.64
RC5	SESW 33-17-73	5/19/98	225	23	10.5	7.72	32.89	22.65	14.43	2.35	3.21	2.84	48.27	3.00	8.01
RC6	NWSE1 1-15-73	10/10/96	54	31	9.6	7.78	54.30	13.70	3.46	0.74	4.58	5.28	18.20	3.37	8.38
RC8	NENE 3-14-73	7/10/96	spring		12.4	7.80	47.90	16.20	5.20	1.04	4.06	6.08	17.70	3.49	8.33
RC9	NWNE 2-16-73	10/10/96	49	5	10.4	7.70	51.50	19.40	4.87	0.83	4.84	7.93	30.70	3.47	9.05
Casper Aquifer samples															
C1	NWSW 1-16-73	5/14/98	34	4	10.1	7.24	43.38	16.83	2.75	0.83	4.70	1.79	6.84	3.30	6.32
C2	NENW 1-16-73	5/19/98	115	43	9.5	7.56	47.92	14.05	1.69	0.58	4.11	1.20	4.72	3.23	6.34
C3	NWSW 31-17-72	6/10/98	185	9	10.2	8.40	34.27	19.18	3.70	1.36	4.36	7.86	10.38	2.76	5.71
C4	NWNW 2-16-73	5/17/98	71	36	10.7	7.58	44.07	16.54	2.48	2.74	4.60	3.49	6.62	3.25	6.40
C5	NWNW 6-16-72	5/19/98	98	42	9.8	7.45	45.61	15.21	1.99	2.87	4.12	3.47	5.44	3.37	6.45
C6	NENW 6-16-72	5/28/98	105	52	12.1	7.63	41.70	16.71	4.40	0.94	4.32	2.86	8.37	3.29	6.43
C7	NWSW 1-16-73	5/20/98	65	29	10.9	7.83	40.14	16.33	3.88	0.97	4.76	2.82	10.11	3.23	6.24
C8	NWNW 1-16-73	5/14/98	80	42	10.4	6.66	38.60	19.47	3.18	1.03	4.50	2.33	9.16	3.31	6.22
C9a	SENW 1-16-73	10/10/96	74	35	10.1	7.83	40.10	19.50	3.68	0.86	5.16	2.65	9.64	3.46	7.87
C9b	SENW 1-16-73	9/15/97	74	35	10.0	7.68	NA	NA	NA	NA	NA	NA	NA	NA	NA
C9c	SENW 1-16-73	10/16/97	74	35	8.9	8.08	39.51	21.18	2.11	0.64	4.31	2.50	9.76	3.47	7.87
C9e	SENW 1-16-73	5/28/98	74	35	9.8	6.74	39.82	18.16	3.01	1.19	4.72	2.26	7.84	3.32	6.25
C10	SENW 1-16-73	5/17/98	80	39	9.1	7.60	40.51	18.52	3.30	1.22	4.73	2.68	8.94	3.30	6.35
C11	NESE1 14-15-73	7/10/96	48	5	8.6	7.72	56.70	14.60	1.95	0.72	3.78	3.61	7.27	3.82	8.48
C12	NESE2 14-15-73	7/10/96	50	4	8.6	7.64	58.30	13.90	2.02	0.62	3.76	3.60	7.37	3.79	8.47
C13	NESE3 14-15-73	7/10/96	49	4	8.5	7.53	53.90	13.00	1.81	0.63	3.55	3.38	7.33	3.81	8.17
C14	NESE4 14-15-73	7/10/96	108	10	8.8	7.59	53.90	13.00	1.88	0.61	3.69	3.56	7.26	3.81	8.18
C15	NWNE 13-16-73	6/4/98	77	10	9.3	8.41	41.87	16.29	5.08	0.81	5.11	4.31	13.18	3.18	6.65
C16	SWSE 23-15-73	7/10/96	38!	14	9.3	7.66	54.40	14.30	2.21	0.65	3.83	2.95	7.88	3.74	8.26
C17a	SWSE 23-15-73	7/10/96	22	3	9.6	7.55	51.70	14.60	2.49	0.69	3.8	2.57	8.48	3.73	8.15
C17b	SWSE 23-15-73	10/11/96	22	3	9.3	7.27	50.20	14.30	2.33	0.69	4.35	2.40	8.52	3.70	8.03
C18	SWSE 23-15-73	7/10/96	26	8	9.1	7.63	47.50	16.30	2.76	0.89	3.98	2.99	9.51	3.66	8.07
C19	SWSE 23-15-73	7/10/96	31	10	9.1	7.62	52.80	14.70	2.61	0.71	3.81	3.37	9.32	3.69	8.23
C20	SWSE 23-15-73	7/10/96	31	20	9.5	7.68	46.90	15.40	2.53	0.78	3.97	2.42	8.51	3.78	8.03
C21a	SWSE 23-15-73	7/10/96	4	2	9.0	7.56	51.40	15.30	3.07	0.86	3.94	4.02	11.30	3.66	8.27
C21b	SWSE 23-15-73	10/11/96	4	2	8.6	7.52	50.00	15.20	2.92	0.89	4.41	3.48	10.20	3.55	8.05
C22	SESE 8-16-72	6/4/98	77	58	7.4	8.38	48.56	12.73	1.49	0.86	3.83	1.34	5.31	3.32	6.37
C23	NWNE 2-16-73	10/10/96	68	3	10.7	7.88	45.90	17.40	4.01	1.03	5.21	3.11	11.90	3.59	8.15
C24	NENE 2-16-73	10/10/96	74	17	11.0	8.06	35.20	12.10	4.55	0.89	5.04	1.63	8.82	2.90	6.33
C25b	NWNE 2-16-73	10/30/97	94	10	8.0	7.58	56.61	12.19	1.52	0.40	3.81	1.79	5.81	3.60	7.92
C26a	NWNE 2-16-73	10/16/97	99	4	7.9	7.64	47.88	17.99	1.73	0.54	4.39	1.53	4.66	3.29	7.65
C26b	NWNE 2-16-73	10/30/97	99	4	8.0	7.60	49.39	16.08	1.63	0.48	4.13	1.53	4.74	3.63	7.90
C27	SWSW 1-16-73	5/20/98	68	30	10.8	8.06	44.14	15.09	2.17	0.81	4.49	1.44	4.54	3.29	6.19
C28a	SWSW 1-16-73	5/14/98	74	40	10.7	6.60	44.32	16.82	2.78	0.80	4.76	1.82	6.23	3.39	6.44
SC28b	WSW 1-16-73	4/1/99	74	40	NA	NA									
C29	NENW 2-15-73	7/10/96	73	0	9.4	7.66	53.30	17.80	2.46	0.83	3.97	3.49	9.85	3.96	8.81
C30a	CNWNE 2-15-73	7/10/96	171	9	9.8	7.69	51.50	16.60	2.05	0.72	3.88	2.22	8.15	3.90	8.43
C30b	NWNE 2-15-73	10/11/96	171	9	8.8	7.81	51.80	17.30	2.08	0.75	4.40	2.62	9.11	3.88	8.55
C30c	NWNE 2-15-73	11/25/96	171	9	9.0	7.79	59.15	19.24	1.87	0.74	4.40	2.51	8.74	2.72	7.88
C30d	NWNE 2-15-73	1/24/97	171	9	9.3	7.75	59.76	19.35	1.85	0.71	4.33	2.53	8.64	4.09	9.29
C31	SWSW 1-16-73	5/14/98	71	41	9.9	7.43	42.20	16.45	2.98	0.79	4.65	1.91	6.61	3.25	6.22
Mixed Casper and Precambrian aquifers samples															
PC2	NENW 3-16-72	6/2/98	142	99	11.0	6.26	43.59	11.98	1.40	1.57	3.78	1.33	2.67	3.13	5.86
PC3a	SENE 5-16-72	9/15/97	123	57	9.8	8.07	47.92	14.04	1.51	3.87	4.18	5.52	6.51	3.73	8.00
PC3b	SENE 5-16-72	5/29/98	123	57	9.9	8.12	47.33	14.49	1.89	0.65	4.10	1.77	7.25	3.29	6.40
PC4a	SWNE 6-16-72	9/15/97	111	46	9.8	7.82	30.59	20.23	2.05	1.40	4.04	2.55	4.60	3.23	6.94
PC4b	SWNE 6-16-72	5/29/98	111	46	12.9	8.06	34.26	19.12	3.39	0.85	4.42	1.82	5.94	3.14	5.71
PC6	SESE 5-16-72	6/4/98	49	no data	9.4	8.46	41.86	20.39	4.53	1.52	4.71	5.58	8.58	3.34	6.63

Table 2 (continued)															
Sample	Location (Sec-Tw-Ra)	Date Collected	Well Depth (m)	Static Water Level (m)	Temper- ature	pH	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Si (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	Alk. (meq/L)	TDI (meq/L)
Precambrian aquifer samples															
P1	SESW 26-15-72	7/3/96	15	3	7.4	7.11	96.70	3.77	2.67	2.22	5.32	32.8	8.19	4.15	10.94
P2	SESE 23-15-72	7/3/96	21	6	6.6	7.16	72.50	2.21	2.06	1.18	3.96	1.86	4.24	3.90	8.12
P3	SENW 29-15-71	7/3/96	11	6	10.7	6.62	13.90	2.94	5.10	2.43	4.92	3.86	10.40	0.89	2.67
P4	SWNE 24-15-72	7/3/96	24	16	14.9	6.80	16.00	2.72	3.34	1.96	5.75	3.08	7.35	0.94	2.70
P5a	NESW 2-16-72	10/16/97	spring		7.3	6.95	43.10	5.60	5.00	0.73	8.54	1.91	13.47	2.75	6.32
P5b	NESW 2-16-72	6/10/98	spring		9.7	8.55	42.00	6.54	6.35	1.06	8.27	1.77	14.38	2.35	6.10
Precipi- tation	SWSE-26-16-73	9/6-7/96			NA	NA	2.34	0.13	0.18	0.22	0.10	0.41	2.11	0.13	0.30
snow 1	SENE 4-16-72	4/30/98			NA	NA	0.77	0.06	0.20	0.32	0.08	0.37	0.18	0.01	0.10
snow 2	NESW 3-16-72	3/19/99			NA	NA									
snow 3	SWNW 36-17-72	3/19/99			NA	NA									
Well depth and static water level information from the Wyoming State Engineer, www.seo.state.wy.us															

(Figure 3). Lundy (1978) suggested that the geochemical character of Precambrian ground waters is due to dissolution of plagioclase feldspars.

Major ion data have been used to identify ground water mixing between the Redbeds and Casper Formation aquifers (Lundy 1978; Huntoon and Lundy 1979; Younus 1992; Mazor et al. 1993). Our data support these identifications. For example, data from this study and from Lundy (1978) both show that the ion concentrations of suspected mixed Redbeds-Casper ground waters fall between those of the end members (Figure 3).

Mixing between the Precambrian and Casper Formation aquifers has not been established in previous studies. This is due in part to the variability of the chemical composition of Precambrian-derived waters. In general, Precambrian and Casper Formation waters exhibit overlapping compositions, with the exception of magnesium (Figure 3). The suspected mixed waters have magnesium concentrations within the range typical of Casper Formation waters. Therefore, the possibility of mixing between the Casper Formations and Precambrian aquifers cannot be evaluated based on major ion data alone.

Strontium Isotopic Character of Aquifers and Ground Waters

Bighorn Basin ground waters exhibit strontium isotopic compositions similar to the aquifers from which they are derived: ground waters from wells in the Madison Aquifer exhibit $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70873 to 0.70941 (Table 3, Figure 4), which overlap with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of two Madison Limestone rock samples (0.70809 and 0.70875). More radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values are characteristic of the Tensleep water sample (0.71220) and analyzed sandstone (0.71123). It appears that ground waters from these two aquifers can be distinguished by their strontium isotopic compositions.

The snow sample from the Bighorn Basin yielded a radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7950, far higher than ratios analyzed for snow elsewhere (Simonetti et al. 2000). We infer that strontium from local eolian, radiogenic Archean-derived detritus has contributed to this sample. The surface flow sample located 5 km downstream of the snow sample

also exhibits a radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7214), suggesting that it, too, contains a radiogenic component contributed by snowmelt and possibly also direct eolian deposition.

In the Laramie Basin, the strontium isotopic compositions of the ground waters also reflect the distinct ratios of their respective aquifers (Table 4, Figure 5). Precambrian-derived waters are the most radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$ = 0.7113 to 0.7940), consistent with the old, high rubidium/strontium granitic rocks present in the Precambrian aquifer. Redbeds waters are the least radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$ = 0.7078 to 0.7091), as is expected of waters interacting with rocks of the Redbeds Group, which have lower rubidium/strontium ratios. Casper Formation waters exhibit intermediate values of ~0.7099 to 0.7105. This narrow range of strontium isotopic compositions is observed in ground waters acquired from very different depths and from various subaquifers within the Casper Formation.

Rain and snow samples from the Laramie Basin display $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are similar to Casper Formation

Table 3
Strontium Isotopic Compositions of Bighorn Basin Waters and Rocks

Water Sample	Description	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr, ppm
Mad 1	Madison spring	0.70926	0.870
Mad 2	Worland city well	0.70941	0.284
Mad 3	Madison spring	0.71619	0.045
Mad 4	Surface flow	0.72135	0.032
Mad 5	Snow	0.79500	0.010
Mad 7	Hyattville city well	0.70873	0.495
Ten 1	Tensleep spring	0.71220	0.418
Rock Sample	Description	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr, ppm
Mad A	Madison paleokarst	0.70875	46.733
Mad B	Madison limestone	0.70809	112.51
Ten A	Tensleep Fm.	0.71123	109.32

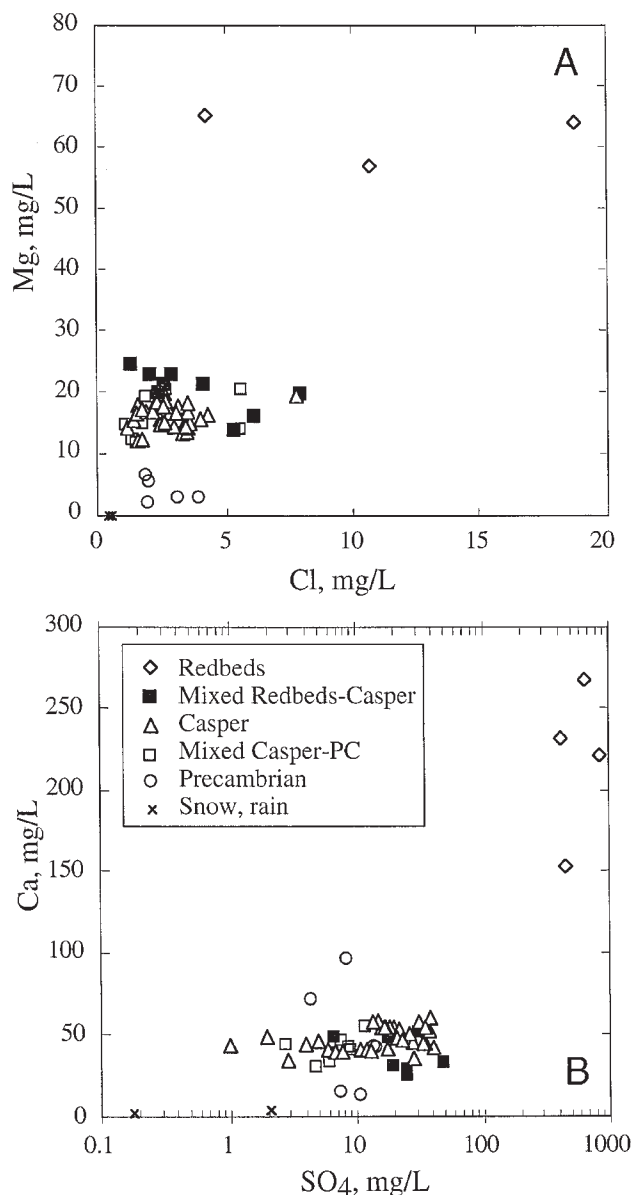


Figure 3. Plots of (a) magnesium content vs. chlorine content and (b) calcium content vs. SO_4 content of Redbeds, Casper Formation, Precambrian, mixed Casper-Precambrian, and mixed Redbeds-Casper ground waters. Low magnesium contents are diagnostic of Precambrian ground waters, whereas Redbed ground waters are characterized by high magnesium, calcium, and SO_4 contents. The intermediate compositions of mixed Redbeds-Casper samples between Redbed and Casper compositions identifies mixing of these two end members in wells open to both aquifers. Samples from wells identified as potentially incorporating ground water from both Casper and Precambrian aquifers have compositions that overlap those of Casper ground waters, hence mixing cannot be identified on the basis of major ion compositions.

ground waters ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7098$ to 0.7107). However, strontium concentrations in local precipitation are extremely low compared to amounts found in ground waters (0.001 to 0.006 ppm vs. 0.07 to 7.85 ppm).

In general, Redbeds ground waters have the highest strontium concentrations (0.89 to 7.85 ppm), whereas Precambrian-derived waters have the lowest concentrations (0.07 to 0.16 ppm). Strontium concentrations in Casper

Formation ground waters range from 0.15 and 0.37 ppm, with an average of ~ 0.2 ppm.

Several wells throughout the Laramie Basin were sampled repeatedly to determine the time-dependence of the strontium isotopic composition of ground water. Analyses of a domestic well near the Spur Monocline (C9) indicate slight variation in the strontium isotopic composition of Laramie Basin ground waters. Five water samples collected from this well between October 1996 and May 1998 yielded $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.71013 to 0.71020 (Table 4, C9a–e), but there does not appear to be a predictable seasonal or temporal trend to the variation.

Other repeated samples did not indicate substantial change in the strontium isotopic composition of Laramie Basin ground waters. For example, four samples (C30a–d) were collected over a seven-month period from the same Laramie municipal well. C30d was collected after a heavy snowstorm in order to compare the strontium isotopic composition of ground waters before and after a period of increased recharge to the aquifer. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all four samples were identical within error: 0.70985 to 0.70986 (Table 4). Several collections during a month-long pumping test of new municipal production wells yielded constant strontium isotopic signatures, $^{87}\text{Sr}/^{86}\text{Sr}$: C25a = 0.71036, C25b = 0.71036, C26a = 0.71035, and C26b = 0.71038 (Table 4). The data from these and other repeat analyses (RC4, C17, C28, P5, PC3, and PC4) are interpreted to suggest that the strontium isotopic compositions of ground waters in the Laramie Basin aquifer system remain relatively constant throughout time, despite external stresses to the aquifer system.

Whole rock samples from each of the three aquifers in the Laramie Basin exhibit distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, with little overlap (Table 4). In general, the Precambrian Sherman and Horse Creek granitic rocks have the most radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7276 to 0.7915), whereas the Redbeds Group has the lowest (0.7084 to 0.7117). Casper Formation sandstones and limestones display intermediate values of 0.7115 to 0.7192. Redbeds and Precambrian-derived rocks generally have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios similar to that of their ground waters. The strontium signatures of these waters encompass nearly the entire range of values exhibited by their respective aquifer rocks. However, Casper Formation sandstones have more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the ground waters extracted from them ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7123$ to 0.7192 vs. 0.7099 to 0.7105). This reflects the fact that the waters do not interact with the strontium in all components of the rock, as demonstrated by the results of step-dissolved samples.

The primary Casper Sandstone sample subjected to stepwise leaching consists of quartz grains covered with substantial amounts of carbonate cement. No feldspar or other detrital minerals were observed. Sequential application of various reagents yielded leaches with varied $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and strontium concentrations (Table 5). The MgCl_2 solution yielded a strontium isotopic ratio typical of Casper Formation ground waters ($^{87}\text{Sr}/^{86}\text{Sr} = 0.71022$). SEM imaging revealed no observable change in the rock. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the NaOAc solution (0.70997) is also indistinguishable from Casper Formation ground waters, but the concentration of strontium in the leachate was much higher than with MgCl_2 . SEM imaging indicated that much

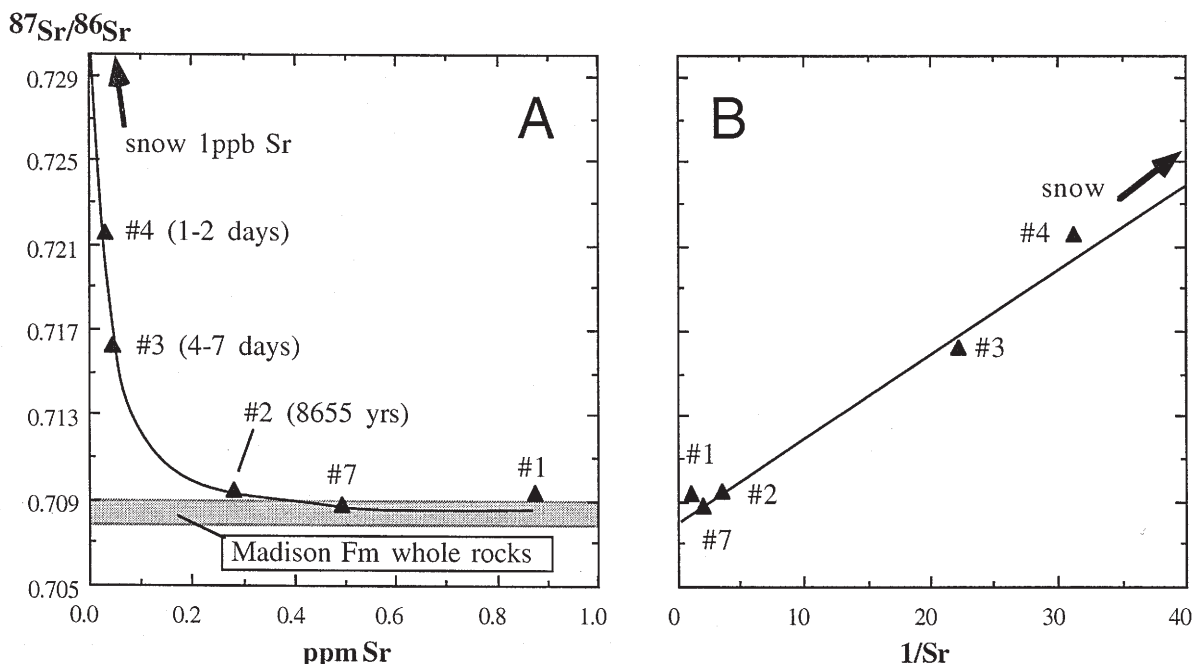


Figure 4. Variation in strontium isotopic ratio and concentration with increased residence time in the Madison Aquifer. (a) Isotopic compositions of ground waters rapidly approach those of the host rock. (b) The linear relationship of these data vs. $1/\text{Sr}$ is consistent with simple two-component mixing between meteoric and Madison isotopic compositions.

of the carbonate cement was dissolved during this step. The application of HCl to the rock sample resulted in an acid leach with a high strontium concentration, but a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio that is slightly lower than previous steps ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70942$). The HCl removed most of the remaining carbonate cement from the sandstone. The series of HF/HNO₃ treatments exhibit very high strontium isotopic ratios, but very low strontium concentrations. These steps removed the small remaining amount of carbonate cement and

severely etched the quartz grains. Therefore, the high $^{87}\text{Sr}/^{86}\text{Sr}$ component must be derived from the most refractory components of the rock, the detrital quartz grains, but is not transferred to the ground water.

A second Casper Sandstone sample from outcrops near the northern end of the study area (Figure 2) was treated sequentially with NaOAc and HCl. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of these leaches (0.70979 and 0.70988, respectively) are similar to those from the first sample, suggesting that the isotopic composition of carbonate cement in the Casper Formation sandstones is fairly uniform across the study site (Table 5).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of carbonates and carbonate cements in Bighorn and Laramie basins' aquifer rocks do not correspond with the $^{87}\text{Sr}/^{86}\text{Sr}$ sea water curve for their respective ages (Mississippian to Triassic, $^{87}\text{Sr}/^{86}\text{Sr} \cong 0.7067$ to 0.7080). This most likely reflects strontium isotopic changes associated with late alteration processes. Mississippian to recent karst development within the Madison Aquifer (Huntoon 1985; Boyd 1993) may have increased the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of those carbonates because the strontium isotopic ratio of nonmarine waters, although variable, is typically more radiogenic than sea water (Faure 1986). The Tensleep Sandstone has undergone several postdepositional cementation events, the most recent one depositing carbonate cements (Mankiewicz and Steidtmann 1979). Because the Tensleep Sandstone is chronologically and petrologically correlative to Casper Formation sandstones, these same cementation events may have affected the strontium composition of both these formations. Therefore, the more radiogenic strontium ratios of the aquifers and ground waters are probably not a product of primary deposition, but instead reflect subsequent diagenetic processes.

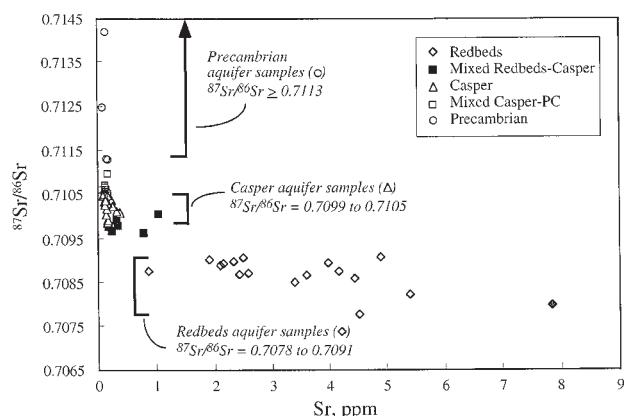


Figure 5. Strontium isotopic ratios and strontium concentrations of Redbeds, Casper, Precambrian, and mixed aquifer ground waters. Precambrian, Casper, and Redbeds ground waters are identified by distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Redbeds ground waters are also distinguished by high (> 1 ppm) strontium concentrations. Ground water samples that may incorporate water from both Precambrian and Casper aquifers (open squares) or Casper and Redbeds aquifers (filled squares) occupy intermediate positions between the two end members on the diagram.

Table 4
Strontium Isotopic Compositions of Laramie Basin Waters and Rocks

Water Sample	⁸⁷ Sr/ ⁸⁶ Sr	Sr, ppm	TU	Water Sample	⁸⁷ Sr/ ⁸⁶ Sr	Sr, ppm	TU
Redbeds Aquifer samples				C25a	0.71036	0.142	
R1	0.70797	7.851		C25b	0.71036	0.147	
R2	0.70821	5.415		C26a	0.71035	0.139	
R3	0.70867	3.604		C26b	0.71038	5.415	
R4	0.70778	4.522		C27	0.71029	0.165	
R5	0.70804	3.401		C28a	0.71022	0.208	
R6	0.70894	3.987		C28b	0.71024	0.216	
R7	0.70899	1.93		C29	0.70986	0.207	
R8	0.70859	4.435		C30a	0.70985	0.187	
R9	0.70874	0.885		C30b	0.70985	0.192	8.98
R10	0.70871	2.587		C30c	0.70985	0.205	
R11	0.70868	2.438		C30d	0.70986	0.177	
R12	0.70906	4.91		C31	0.71023	0.200	
R13	0.70875	4.165		Mixed Casper and Precambrian aquifer samples			
R14	0.70898	2.346		PC2	0.71050	0.105	
R15	0.70892	2.16		PC3a	0.71067	0.126	
R16	0.7089	2.103		PC3b	0.71069	0.127	
R17	0.70909	NA		PC4a	0.71053	0.165	
R18	0.70907	NA		PC4b	0.71056	0.158	
R19	0.70906	2.5		PC6	0.71096	0.169	
Mixed Redbeds and Casper aquifer samples				Precambrian aquifer samples			
RC1	0.70978	0.332		P1	0.71421	0.156	
RC2	0.70991	0.312		P2	0.71249	0.078	
RC3	0.70981	0.331		P3	0.79400	0.067	
RC4a	0.70971	0.234		P4	0.73948	0.069	
RC4b	0.70968	0.250	0.00	P5a	0.71130	0.162	
RC5	0.70963	0.778		P5b	0.71132	0.156	
RC6	0.70977	0.169	14.00	Precipitation	0.70982	0.006	
RC7	0.71008	1.030		Snow	0.71012	0.001	
RC8	0.71023	0.227	6.18	Snow	0.71022	0.002	
Casper Aquifer samples				Snow	0.71071	0.001	
C1	0.71025	0.192		Rock Sample	Description	⁸⁷Sr/⁸⁶Sr	Sr, ppm
C2	0.71039	0.124		LaPrele 1 25–45	Chugwater Fm.	0.70897	9.908
C3	0.71039	0.190		LaPrele 1 80–85	Forelle Fm.	0.70844	7.061
C4	0.71025	0.163		LaPrele 1 165–170'	Satanka Fm.	0.70888	37.858
C5	0.71046	0.135		LaPrele 1 270–280'	Satanka Fm.	0.71170	8.431
C6	0.71046	0.184		LaPrele 1 450–470'	Casper Fm. ls	0.71150	4.961
C7	0.71018	0.256		LaPrele 1 530–550'	Casper Fm. ss	0.71873	0.785
C8	0.71021	0.178		LaPrele 1 590–610'	Casper Fm. ss	0.71924	1.001
C9a	0.71013	0.207	1.22	LaPrele 1 625–640'	Casper Fm. ls	0.71153	1.860
C9b	0.71020	0.184		LaPrele 1 660–680'	Casper Fm. ss	0.71234	2.815
C9c	0.71019	0.190		LaPrele 1 760–780'	Casper Fm. ss	0.71870	1.155
C9d	0.71020	0.205		LaPrele 1 820–840'	Casper Fm. ss	0.71705	0.987
C9e	0.71016	0.203		LaPrele 1 860–880'	Casper Fm. ss	0.71830	0.893
C10	0.71023	0.181		91PH1*	Sherman Granite	0.79150	119
C11	0.70999	0.168		91SMW28*	Sherman Granite	0.74054	180
C12	0.71007	0.151		90SMW5*	Sherman Granite	0.74434	212
C13	0.71005	0.153		90SMW9*	Sherman Granite	0.72764	214
C14	0.71009	0.150		KM9‡	Horse Ck.		
C15	0.71033	0.248			anorthosite	0.70505	328
C16	0.71026	0.184		KM9‡	Horse Ck.		
C17a	0.71026	0.147			anorthosite	0.72997	178
C17b	0.71024	0.150	8.36	LAC87-6‡	Horse Ck. granite	0.74662	180
C18	0.71014	0.268		*Data from Frost et al. 1999			
C19	0.71016	0.186		‡Data from Frost et al. 2000			
C20	0.71026	0.181					
C21a	0.71009	0.336					
C21b	0.71007	0.368	9.10				
C22	0.71033	0.110					
C23	0.71024	0.273					
C24	0.71031	0.192					

Table 5
Results of Step-Dissolution Procedure
Applied to Casper Formation Sandstone

Reagent	Phase Attacked	$^{87}\text{Sr}/^{86}\text{Sr}$ of Solute	Sr Conc. of Solute
1M MgCl_2	Exchangeable	0.71022	0.529 ppm
1M NaOAc	Carbonate	0.70997	3.486 ppm
1M HCl	Carbonate	0.70942	9.096 ppm
HNO_3 -HF	Silicates	0.71326	0.041 ppm
HNO_3 -HF	Silicates	0.71267	0.026 ppm
HNO_3 -HF	Silicates	0.71598	0.014 ppm
Northern Casper Sandstone sample			
1M NaOAc	Carbonate	0.70979	5.958 ppm
1M HCl	Carbonate	0.70989	1.939 ppm

Discussion

Timescale of Strontium Isotope Acquisition

Bighorn Basin

Bighorn Basin samples have variable residence times within the Madison Aquifer. Estimated residence times that follow are based upon dye tracing experiments by Vietti (1977). Stream sample Mad4 has a residence time of only one to two days from its headwaters. This water then flows through an underground paleokarst cave system and is discharged (sample site Mad3) within a week (Figure 1b) (Vietti 1977). Based upon their location at greater distances from the recharge zone, Mad1, Mad2, and Mad7 are inferred to have much longer residence times. This inference appears valid from C-14 dating of Mad2, a sample from the well farthest west into the basin that presumably samples the oldest ground water, which yielded a C-13 corrected age of 8655 ± 335 years (Cline 1995). The strontium isotopic data from these samples form a binary mixing trend between recharge and much older Madison Aquifer ground waters (Figure 4). This trend indicates that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of young Mad3 ground water changed from 0.79500 (the composition of strontium from snowpack at the headwaters of Dry Medicine Lodge Creek) to 0.72135 (the ratio of surface flow in the upper reaches of the creek) to 0.71619 (the isotopic composition of water emerging from subterranean flow) within the one-week travel time suggested by dye tracing. The isotopic composition of this last water sample approaches the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of Madison Aquifer waters with much longer residence times ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70941$). Although more ground water age constraints are required to quantify the time required for final equilibration of strontium between ground water and Madison Aquifer rock, these results are interpreted to suggest that ground waters within carbonate aquifers begin to acquire their strontium isotopic signatures very quickly as strontium is introduced from aquifer rocks into dilute recharge.

Laramie Basin

Tritium levels in seven Casper Formation water samples, sampled and analyzed in 1996, range from 0 to 14 TU

(Table 4). These values reflect variations in the average age of ground waters within the aquifer; values > 5 TU suggest the incorporation of some bomb-era water. These data are interpreted to suggest that the water sample with the highest tritium concentration of 14 TU was recharged after commencement of aboveground nuclear testing some 50 years ago. The other Laramie Basin water samples, with TU from 6.18 to 9.10, also have an average age of < 50 years. Wells C9 and RC4 have lower tritium contents of 1.22 and 0, respectively. Well C9 is interpreted as containing a mixture of pre-1953 water and post-1953 water. Water from well RC4 incorporates no bomb-era tritium.

Although Casper Formation waters exhibit a range of tritium concentrations, there is little variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of these same water samples, $^{87}\text{Sr}/^{86}\text{Sr} = 0.70985$ to 0.71024 (Table 4). The fact that Casper Formation ground waters have similar strontium isotopic ratios regardless of their ages strongly suggests that ground waters in this aquifer acquire strontium from their host rocks on a timescale shorter than the age of the youngest water sampled, that is, in < 50 years.

Strontium Isotope Equilibration Rates in Carbonate vs. Silicate Aquifers

Results presented in this study indicate that ground waters in carbonate or carbonate-cemented aquifers acquire their strontium signatures in a relatively short period of time. The strontium isotope data from the Bighorn Basin indicate that in less than a week, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ground water approaches that of the Madison Aquifer. In addition, the tritium and strontium isotope data from the Laramie Basin are interpreted to suggest that Casper Formation waters acquire their strontium isotopic composition within, at most, decades. Therefore, longer residence time within a carbonate or carbonate-cemented aquifer does not appear to greatly affect the strontium isotopic composition of ground water.

However, the acquisition of strontium by ground water may operate on a different timescale in noncarbonate-bearing rocks. Several studies have shown that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ground waters within granitic rocks are initially the result of interaction with plagioclase feldspar, resulting in low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios compared to whole rock signatures (Edmunds et al. 1984; Edmunds et al. 1987; Kay and Darbyshire 1986; Franklyn et al. 1991; Li et al. 1989; McNutt et al. 1990; Siembille et al. 1998). As residence time within these aquifers increases, the initially low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ground water will also increase as the water begins to dissolve potassium feldspars and micas (McNutt et al. 1990; Bullen et al. 1996; Blum and Erel 1997). Johnson et al. (1997) identified a flowpath within the Snake River Plain basaltic aquifer along which the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the ground water does not change significantly. They suggested that rapid flow rates along this path prevented the ground water from acquiring strontium signatures typical of the rocks. These results indicate that a longer residence time is necessary for ground water to reach equilibrium with crystalline aquifer rocks.

In addition, low permeabilities associated with igneous and metamorphic rocks may also slow ground water equilibration rates. McNutt et al. (1990) suggest that waters

stored within fractures are in contact with the same volume of rock for extended periods of time. This lack of mobility therefore limits the mineral phases with which the ground water can react, and slows the rate of equilibration with the aquifer rock. Slow equilibration rates may affect ground waters in Laramie Basin's Precambrian aquifer. The Sherman Batholith has low intergranular permeabilities (Lundy 1978), but is highly fractured, suggesting that this aquifer's ground water reserves are stored almost completely within fracture zones. This study demonstrated that the Precambrian-derived ground waters exhibit high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that correlate well with those of the granite. Therefore, the ground water probably has had an extended residence time within the Precambrian aquifer in order to achieve a strontium isotopic signature similar to that of the aquifer rocks.

Strontium Isotope Identification of Ground Water Mixing

Because of the variation of the strontium isotopic ratio in ground waters from different waters, the strontium isotopic ratio should be a sensitive monitor of ground water mixing processes. We can evaluate this possibility in the Laramie Basin, where a number of well water samples have been shown to be mixtures of waters from the Casper and Redbeds aquifers (Mazor et al. 1993). The strontium isotopic ratio and strontium concentration of these mixed Casper-Redbeds water samples are plotted in Figure 6, along with samples from the Casper and Redbeds aquifers.

The fraction of strontium (F_{Sr}) derived from each of two end members can be determined from the strontium isotopic ratio of the mixture and the two end members:

$$F_{\text{Sr}} = \frac{{}^{87}\text{Sr}/{}^{86}\text{Sr}_{(\text{mixture})} - {}^{87}\text{Sr}/{}^{86}\text{Sr}_{(\text{end member 1})}}{{}^{87}\text{Sr}/{}^{86}\text{Sr}_{(\text{end member 2})} - {}^{87}\text{Sr}/{}^{86}\text{Sr}_{(\text{end member 1})}}$$

Assigning the average Redbeds component as end member 1 with a strontium isotopic ratio of 0.7087, and the Casper component as end member 2 with a strontium isotopic ratio of 0.7102, we calculate from their strontium isotopic ratios that as much as 40% of the strontium in the mixed Casper-Redbeds water samples is derived from the Redbeds end member. This result does not directly give the volume or mass fraction of water that is derived from the Redbeds Aquifer, rather it simply represents the fraction of the strontium derived from this end member. However, the volume proportion of Redbeds water can be estimated using both the strontium isotopic ratio and the strontium concentrations of the two end members using straightforward binary mixing equations. Using these equations, a hyperbolic mixing line is constructed between an average Casper Formation value ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710$, 0.2 ppm strontium) and an unradiogenic Redbeds water sample, R1 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7080$, 7.851 ppm strontium). Plots of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/\text{Sr}$ yield straight mixing lines (Figure 6). Because of end member variability and because strontium may not behave conservatively as is assumed for simple binary mixing, a single mixing line is not adequate to describe the strontium isotopic and concentration data. However, the expected effects of mixing on the strontium characteristics of ground water samples are clear. Because of the high strontium concentration of Redbeds Aquifer waters compared to Casper Aquifer waters, the strontium isotopic ratios of mixed

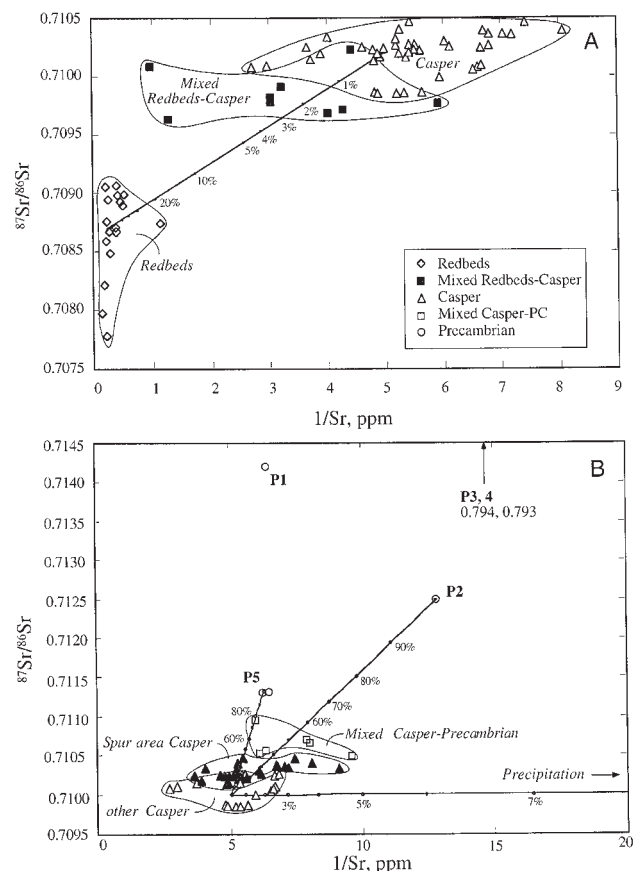


Figure 6. Strontium isotopic ratios and $1/\text{Sr}$ concentrations of (a) Redbeds- and Casper-derived ground waters and (b) Casper- and Precambrian-derived ground waters. Also shown are binary mixing lines between average Redbeds and Casper ground waters (Figure 6a) and binary mixing lines between average Casper, and various Precambrian and meteoric water end members (Figure 6b). If each end member had a single strontium isotopic composition and strontium concentration, and if strontium behaved conservatively, then mixed waters would lie along the mixing lines. However, each aquifer yields water samples with a range in $^{87}\text{Sr}/^{86}\text{Sr}$ and strontium concentrations, and strontium may not be conservative. Therefore, samples identified as mixtures do not lie along any single mixing line. Nevertheless, mixed Redbeds-Casper waters are displaced from Casper compositions towards Redbeds compositions, and the observed displacement may be due to the addition of 5% or less Redbeds water. Likewise, wells tapping both the Precambrian and Casper aquifers exhibit $^{87}\text{Sr}/^{86}\text{Sr}$ higher than Casper Aquifer samples. In addition, the Casper Aquifer in the Spur Monocline area north of Laramie exhibit $^{87}\text{Sr}/^{86}\text{Sr}$ ratios slightly higher than Casper samples elsewhere. Both Spur-area Casper wells, and mixed Casper-Precambrian wells, are interpreted as incorporating Precambrian-derived ground water.

waters are strongly affected by small proportions of the Redbeds end member. The samples containing as little as 2% Redbeds water by volume can be identified readily by their lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Figure 6a). Due to the high strontium contents of Redbeds aquifer waters, addition of < 5% Redbeds component produces the observed shift to lower $^{87}\text{Sr}/^{86}\text{Sr}$ compared to Casper Aquifer waters.

This estimate of 5% or less Redbeds end member in the Casper-Redbeds mixed water samples compares well with estimates based on the SO_4 contents of Casper,

Redbeds, and mixed waters. Taking 5 ppm SO_4 as typical of Casper Aquifer waters and 1500 ppm SO_4 as representative of Redbeds waters, the intermediate SO_4 concentrations of the mixed waters suggest that they contain up to 3% Redbeds component. Because of the variability in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, strontium concentrations, and SO_4 contents of Redbeds waters ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70778$ to 0.70909 , strontium = 2.1 to 7.9 ppm, and $\text{SO}_4 = 438$ to 1580 ppm [Tables 2 and 4]), a perfect correlation between the proportions based on SO_4 content and the proportions based on $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is not expected. Moreover, these calculations depend upon correct characterization of strontium and SO_4 concentrations, which may change as a function of dissolution and precipitation of minerals along the flowpath. Nevertheless, their general correspondence demonstrates that strontium isotopic compositions of ground water can be used to identify mixing between aquifers, even when the proportion of one of the end members is small (Figure 6a).

Several wells near the Spur Monocline (PC2–4, PC6) may possibly contain mixed Casper Formation–Precambrian water based upon their well completion records and proximity to Precambrian outcrops. In addition, the highly fractured nature of the rocks in the Spur Monocline area may increase hydraulic connectivity between the Casper Formation and the Precambrian basement. A possible component of Precambrian aquifer water in these wells had not been previously postulated nor evaluated due to (1) the assumption that the Precambrian is a poor producer and (2) the chemical similarity of the Casper Formation and Precambrian aquifers.

When these waters are plotted on a diagram of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. strontium concentration (Figure 6b), it is clear that these Spur area waters are characterized by higher $^{87}\text{Sr}/^{86}\text{Sr}$ than are other Casper Aquifer waters. Assuming that the higher strontium isotope ratios are due to the introduction of Precambrian aquifer water into these wells, then the fraction of strontium from the Precambrian end member can be calculated as for the mixed Casper-Redbeds waters mentioned earlier. The fraction of strontium calculated depends strongly on the strontium isotopic ratio used to represent the Precambrian end member and that water samples from the Precambrian aquifer have higher variable $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.7113 to 0.7940. Taking as an example an intermediate ratio of 0.7125 (sample P2), calculated fractions of strontium from Precambrian aquifers range from 20% to 38%. Estimates of the volume of Precambrian aquifer water that contains this fraction of strontium can be made using binary mixing equations (Faure 1986). Because of the variability of strontium isotopic compositions of Precambrian ground waters, several mixing lines are shown in Figure 6b. Samples representing the Precambrian aquifer include samples P2 and P5. A value of $^{87}\text{Sr}/^{86}\text{Sr} = 0.710$ and 0.2 ppm strontium was used to represent the Casper Aquifer. Most of the suspected Casper-Precambrian mixed water samples lie near one or the other of these mixing lines. If more Precambrian aquifer samples were analyzed and additional mixing lines constructed, then it is possible that mixing lines may encompass the compositions of all mixed samples. We note that one water sample, PC6, plots directly on the mixing line between the Casper Formation and Rogers Canyon spring sample P5. Well PC6 is situated

to intercept westward-flowing ground waters that originate in the Precambrian aquifer near spring P5. The binary mixing calculations suggest that this and the other suspected mixed Casper-Precambrian waters may contain roughly between 40% and 80% Precambrian water by volume.

In fact, many water samples previously considered to be entirely from the Casper Aquifer appear to contain a small fraction of Precambrian water (Figure 6b). Ground waters from wells north of Laramie in the Spur area (filled triangles in Figure 6b) have $^{87}\text{Sr}/^{86}\text{Sr} \geq 0.7102$. This elevated ratio may be due either to (1) a different strontium isotopic composition of the Casper Formation in this area, such that water-rock interaction yields water with a different strontium isotope ratio, or (2) the Precambrian aquifer may be contributing water to wells in this area. The first alternative seems the less likely because rock-leaching experiments on Casper Sandstone from the Spur area yielded the same results as rocks farther south, and because water samples with $^{87}\text{Sr}/^{86}\text{Sr} \geq 0.7102$ are not restricted to the Spur area. These higher values are associated with wells located near major structures and faults (as are those in the Spur area), which may be especially likely to incorporate water from the underlying Precambrian aquifer.

Finally, a mixing line between the Casper Formation and a snow sample is also shown in Figure 6b. Because of the extremely low strontium concentrations of snow, local precipitation contributes little to the strontium isotopic composition of ground waters.

Recovery of Strontium Isotopic Composition of Ground Waters by MgCl_2 Leaching of Aquifer Rocks

The step dissolution experiment performed on a sample of Casper Sandstone revealed a method for recovering the $^{87}\text{Sr}/^{86}\text{Sr}$ signature of ground water previously in the aquifer. The MgCl_2 leach yielded a strontium isotopic ratio that is typical of Casper Formation ground waters. This suggests that the MgCl_2 , which extracts strontium from the mineral surfaces, recovered the strontium isotopic signature of ground water that was once in contact with the sandstone. Because the strontium isotopic ratio of ground water is dependent only upon dissolution of material from rocks and is not affected by mass fractionation or precipitation processes (Peterman et al. 1992; Johnson and DePaolo 1997), the recovered $^{87}\text{Sr}/^{86}\text{Sr}$ ratio should reproduce that of the original ground water. Therefore, MgCl_2 leaches may be a method by which to retrieve the strontium isotopic record of hydrologic processes in settings where it is not possible to directly sample ground water.

Workers in the petroleum industry are presently using recovered strontium isotopes. Smalley et al. (1992) developed the strontium residual salt analysis (SrRSA) technique, which leaches strontium from residual salts within the pores of core samples. This method involves adding ultrapure water to crushed core samples from different reservoirs to produce reconstituted formation waters. By comparing the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the reconstituted waters to each other and to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the reservoir rocks, Smalley et al. (1992), Smalley et al. (1995), and others (Sommer and McBride 1998; McBride et al. 1995; Mearns et al. 1995) using SrRSA were able to determine not only the sources of the formation waters, but also the extent of

hydraulic connectivity between reservoirs. Such source and reservoir communication information is vital for oilfield development and production. Because of the similarity between MgCl_2 and SrRSA techniques, the MgCl_2 procedure described in this study may be used to obtain similar information in hydrogeologic settings, and may be most useful where it is not possible to directly sample ground water.

Conclusions

The results of this study address several aspects regarding the applicability of strontium isotope identification of ground water sources and processes, including whether ground waters from different aquifers have distinct strontium isotopic fingerprints, the timescale on which the strontium isotopic signature is imparted to ground waters in carbonate or carbonate-cemented aquifers, and the identification of mixing of ground waters, particularly in cases where major ion chemistry fails to discriminate ground waters from different aquifers.

Strontium Isotopes as a Fingerprint for Ground Water

The strontium isotope system can identify subtle differences in rock chemistry that may in turn be imparted to ground waters interacting with rock. The aquifers in the Laramie and Bighorn basins exhibit distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, well outside the precision of the ratio measurement (± 0.00001). Their individual strontium isotopic compositions are due to differences in the ages and compositions of the aquifers. For example, the Laramie Basin Precambrian aquifer's potassium-rich mineral phases such as potassium feldspar readily incorporate ^{87}Rb , the parent isotope of ^{87}Sr , into their chemical structure. Radioactive decay of this ^{87}Rb for 1.4 B.Y. results in a highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. On the other hand, the Redbeds and Casper Formation aquifers have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios because they are younger and have lower rubidium/strontium ratios. Therefore, the rock types within an aquifer system can be easily distinguished by their strontium isotopic signatures.

More importantly, these distinct strontium isotopic compositions are also present in ground water. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ground waters from the Bighorn and Laramie basins reflect the strontium compositions of the aquifers from which they are derived. This is important for hydrogeologic investigations because otherwise chemically similar ground waters can be distinguished by their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. For example, with the exception of magnesium content, Casper Formation and Precambrian ground waters exhibit virtually identical major ion compositions. In this case, strontium isotopes are far more sensitive indicators of ground water sources than traditional geochemical analyses.

Rate of Acquisition of Strontium Isotopic Fingerprint by Ground Waters in Carbonate or Carbonate-Cemented Aquifers

This study documented the strontium isotopic ratio of waters of varying ages in both the Bighorn and Laramie basins in an attempt to determine the timescale by which

the strontium isotopic ratio is imparted from rock to ground water. Results from the Bighorn Basin suggest that the strontium isotopic ratio changes quickly as strontium is introduced from carbonate aquifer rocks into dilute recharge. There, a significant shift in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from $^{87}\text{Sr}/^{86}\text{Sr} = 0.72135$ to 0.71619 was observed between the time that surface water entered the Madison Aquifer and the time it emerged in springs ~1 week later. In the Laramie Basin, ground water samples from the Casper Aquifer had varying tritium contents (TU = 0 to 14) suggesting that whereas samples with higher tritium contents contained bomb-era water, other samples predated the nuclear age. However, there was no correlation between apparent ground water age and strontium isotopic composition, suggesting that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was imparted from this carbonate-cemented sandstone aquifer to ground water on a timescale shorter than the age of the youngest water samples, that is, in $< \sim 50$ years.

Identification of Ground Water Mixing

The present study also used strontium isotopes to confirm previously identified mixing of ground waters and to detect unsuspected mixing between aquifers. Laramie Basin Redbeds waters have high SO_4 , magnesium, chlorine, and calcium contents that distinguish them from other Laramie Basin ground waters. Mazor et al. (1993) used these chemical parameters to determine the proportions of Redbeds waters in mixed Redbeds-Casper samples. These proportions were reproduced by mixing calculations based on the strontium isotopic compositions of these same waters.

Significantly, strontium isotopic identification of mixing was successful where major ion approaches failed. Water samples collected from the Casper Aquifer in the Spur area of the Laramie Basin exhibit increasingly higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with increased proximity to Precambrian outcrops. These more radiogenic values are interpreted to be the result of mixing with progressively greater proportions of Precambrian water near the Casper Formation–Precambrian contact. This suggests that extensive interaction exists between the Precambrian and Casper Formation aquifers. Faults and fractures that extend into the basement rocks are the probable conduits for ground water transport between the two aquifers. Therefore, the Precambrian aquifer should be considered an important contributor to the Laramie Basin aquifer system, especially near the Spur Monocline.

In summary, the results of this study demonstrate the utility of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in identifying the source of ground waters, ground water flowpaths, and interaquifer communication, and suggest that more widespread use of the strontium isotopic fingerprint is warranted.

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